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COMMISSION ON COLLOID AND SURFACE CHEMISTRY  
INCLUDING CATALYSIS\*  
SUBCOMMITTEE ON CATALYST CHARACTERIZATION†

# MANUAL ON CATALYST CHARACTERIZATION

(Recommendations 1991)

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## 1. INTRODUCTION

This manual has been prepared by the Commission on Colloid and Surface Chemistry including Catalysis of the IUPAC. It results from the general feeling among surface and catalysis chemists both from academia and industry that the rapid increase of knowledge in science of catalysis and the better understanding of the mechanism of catalytic processes is not accompanied by the development of the appropriate scientific language. Many terms, widely used in the literature, remain vague and undefined. Thus, the Subcommittee on Catalysis was created with the task of preparing a catalyst characterization chart, listing all parameters which should be specified in order to obtain a full description of a catalyst, and of formulating the definitions of these parameters as well as recommendations concerning the terminology.

The present manual is based on the same general principles as those used in the Manual of Symbols and Terminology for Physicochemical Quantities and Units of the Commission on Symbols, Terminology and Units of the Division of Physical Chemistry, Definitions, Terminology and Symbols in Colloid and Surface Chemistry of the Commission on Colloid and Surface Chemistry, Appendix II Part I Definitions, Terminology and Symbols in Colloid and Surface Chemistry, Part II Heterogeneous Catalysis, and Recommendations in Reporting Physisorption Data for Gas/Solid Systems. (ref. 1-3)

Since the present proposals should be considered as one of the sub-sets of the terms and symbols of physical chemistry, the general principles are not repeated here. (see Note a)

This manual provides definitions and recommendations concerning the terminology of catalysis. It should be read in conjunction with the Manual of Methods and Procedures for Catalyst Characterization which provides details and recommendations concerning the experimental methods used in catalysis.

## 2. CATALYST FORMULATION AND METHODS OF ITS PREPARATION

### 2.1 Methods of preparation

Many catalysts consist of an active component or components (see 2.2) deposited on a support (such as silica, alumina, carbon). The role of the support may be to improve the properties (e.g. stability) of the active component(s), or to participate directly in the catalytic reaction (e.g. by providing acidic sites). The following terms define general preparation methods.

#### 2.1.1 Precipitation

Precipitation is a method often used for producing both support precursors and catalyst precursors (including precursory forms of zeolites) and occurs when two or more solutions are mixed in a suitable way. In addition to providing general details of the method (e.g., concentration, temperature, pH, etc.) it is necessary to indicate specifically the order and rate of addition of one solution into the other, a description of the mixing procedure and the details of the ageing procedure, if any. The association of two or more active elements in the precipitate, in a single or several phases, may be achieved by co-precipitation.

#### 2.1.2 Deposition

Deposition describes the application of the catalytic component (e.g. nickel, as nickel nitrate) on to a separately produced support (e.g. silica). Any treatment of the support before the deposition step must be described precisely.

Deposition may be achieved by impregnation, i.e., contacting the support for a specified time with a solution containing the active elements. When the active elements are contained in a volume of solution corresponding to the pore volume, the procedure is called dry or pore volume impregnation. The term incipient wetness method is used to describe impregnation when the volume of the solution is empirically determined as corresponding to that beyond which the catalyst begins to look wet. One or several parallel processes such as adsorption, ion exchange, selective reaction on or with the surface of the support may take place during impregnation. Sometimes the

**Note a:** Revised and extended edition of the aforementioned 'Manual' has been published as a book under the title *Quantities, Units and Symbols in Physical Chemistry* (Blackwell Scientific Publications, Oxford, 1988).

process of impregnation is carried out by percolation of the impregnating solution through a bed of support, or by dipping the support in the impregnation solution.

Two or more active elements may be introduced either in a single step by co-impregnation or subsequently one after the other in successive impregnations. Drying and often calcination (see 2.1.5) take place between impregnations. Deposition involving the formation of a strong (e.g. a covalent) bond between the support and the active element is usually described as grafting or anchoring. This is achieved through a chemical reaction between functional groups (e.g. hydroxyl groups) on the surface of the support and an appropriately selected inorganic, or organometallic compound of the active element. When deposition takes place by adsorption or reaction from the gas phase, the term chemical vapour deposition is used.

Sometimes a special technique of precipitation-deposition is used, in which an active element (e.g. nickel) is deposited onto a carrier (e.g. silica) in suspension in the precipitating solution (e.g. nickel nitrate) by slow addition, or in situ formation (e.g. of OH<sup>-</sup> by hydrolysis of urea) of a precipitating agent.

Ion exchange, which as already mentioned may occur during impregnation, is an important process in the synthesis of zeolites and also in the preparation of some supported metal catalysts.

### 2.1.3 Encapsulation

Enzymes or cells, which are of relatively large size may be entrapped in a maze of polymeric molecules (a gel). This procedure is called immobilization by inclusion. When the biocatalyst is enclosed inside a semipermeable membrane, usually approximately spherical, the method is known as encapsulation. In the process of reticulation the primary biocatalyst particles (individual enzyme molecules, cofactors or individual cells) are covalently attached to each other by organic chains, into a three-dimensional network. The term grafting is also used in this context. Attachment to the support by adsorption forces is called immobilization by adsorption.

### 2.1.4 Selective removal

Preparation of the catalyst by the reaction of a precursor (e.g. NiAl alloy) with a reactant (e.g. an aqueous NaOH solution) which selectively dissolves part of the precursor (Al) leaving the active agent (Ni) is described as selective removal method.

### 2.1.5 Treatment of intermediate solids or precursors

Very often the intermediate solid is left for some time under specified conditions in the presence of the impregnating or precipitating mixture. This is called ageing. Washing of the intermediate solids formed by precipitation is generally required to remove adsorbed ions such as Na<sup>+</sup> which were introduced during the precipitation.

The solvent may be eliminated without chemical transformation by drying. Many different processes may be applied to this end such as drying in an oven, fluidized bed drying, spray drying, freeze drying.

The intermediate solids are usually subjected to heat treatment, sometimes called calcination. The term calcination should only be used when heating is carried out in air or oxygen. It is essential to describe the exact conditions of heat treatment, in particular the condition of the introduction of the sample, temperature and the rate of its change, pressure, gas flow conditions, etc. Chemical transformation of the solid may take place in the course of the heat treatment. When this transformation proceeds without interaction with the atmosphere the term thermal decomposition may be used.

### 2.1.6 Activation of the precursor

The final step in the preparation of a catalyst is the transformation of the precursor to the active phase (e.g. metal, sulfide) which is sometimes called activation. The activation may be a reduction (e.g. by H<sub>2</sub>), reduction-sulfidation (e.g. by H<sub>2</sub> + H<sub>2</sub>S), dehydroxylation (e.g. by removal of H<sub>2</sub>O from zeolite) or oxidation (e.g. by O<sub>2</sub>). The details of the activation

process must be stated (e.g. partial pressure and purity of gas, method of heating and its rate, gas reacting flow rate, sample size).

## 2.2 Chemical composition

Catalytic materials are frequently composed of many components and phases. Therefore, it is seldom adequate to define a catalyst by merely stating the chemical composition, e.g. 1% Pt, 99% SiO<sub>2</sub>. Note that by convention the support should be indicated clearly by using an oblique stroke (*solidus*), e.g. 1% Pt/SiO<sub>2</sub>.

The term major active component may be used to describe the active component, the proportion of which greatly exceeds that of the others. Secondary components added on purpose may be described as additives, whereas the term impurities should be reserved for trace amounts of other elements, over which the investigator (manufacturer) has little control. The use of the word promoter implies that the additive improves some particular property of the catalysts, and it is desirable to indicate this property when known (e.g. activity, selectivity, textural properties, resistance to sintering). The term modifier is used sometimes in this context, but is not recommended. The term modifier is used in a special and proper sense in the context of asymmetric hydrogenation when, for example, Raney nickel is modified by optically active tartaric acid in order to impart the property of asymmetry to hydrogenation reactions over the catalyst.

The action of adding a small amount of foreign atoms to form a solid solution in the lattice of a nonmetallic catalyst is sometimes called doping.

The description of the composition of a catalytic system should indicate the crystallographic form of the support (e.g.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> - anatase). The chemical composition should be unambiguously defined. When specifying the proportions of the active phase to the support, weights may be used provided the stoichiometry is clearly indicated (e.g. Co<sub>3</sub>O<sub>4</sub> and MoO<sub>3</sub>, Co<sub>9</sub>S<sub>8</sub> and MoS<sub>2</sub>, NiO, Pt).

## 2.3 Aggregate morphology

The solid obtained after the operations described in Section 2.1 (supports, intermediate solids, precursors or catalysts) can be used as such (e.g. powders) or shaped into larger entities (beads, pellets, extrudates, rings). In special cases structures called monoliths are used as support. Description of the aggregate morphology should include reference to the crystal structure and details of the shape of the particles of the various phases present, their arrangement in space (including the voids or pores) and the shape of larger physically separate entities. The structure is defined by the distribution in space of the atoms or ions in the material part of the catalyst, the texture is defined by the detailed geometry of the void space in the particles of catalyst and by the spatial relationships between the different phases present.

Certain materials used as catalysts or supports consist of spheroids smaller than 10 nm in diameter, cemented into larger entities. A primary particle should be defined as the smallest discrete identifiable entity and the method of identification should be mentioned (e.g. transmission electron microscopy, scanning electron microscopy). An assemblage of such primary particles exhibiting an identifiable collective behaviour (e.g. chemical nature of the aggregated primary particles, texture of the aggregate, resistance to mechanical separation upon grinding) constitutes an aggregate. When describing the aggregates the criterion of identification should be mentioned. Strongly bonded aggregates are called agglomerates.

A collection of loose, unattached, primary particles or aggregates of relatively small size is usually called a powder. It is recommended that the word powder is used if the largest dimension of the individual entities is smaller than 1 mm. The shape of the particle should be described (sphere, flake) and the method of its preparation specified (crushing, grinding spray drying).

In the designation of larger aggregates two criteria may be used: shape, referring to geometrical definition, or method of preparation. Spherical, spheroidal or rounded aggregates obtained by beading or granulation are called beads, and aggregates of cylindrical shape, formed by tableting